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Quantum mechanical study of the electronic spectra, torsional potential and physico-chemical properties of rotational conformers of methyl vinyl ketone in different electronic states

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Abstract : Methyl vinyl ketone (MVK) molecule may be considered as a two rotor system in which internal rotation may take place about a C-C single bond connecting two completely asymmetric moieties $CH = CH_2$ and $O = CCH_3$ and also about $C–CH_3$ bond leading to hindered rotation of the methyl group Semi-empirical quantum chemical calculations in MNDO approximations using modified AM1 Hamiltonian and CNDO/2 approximations for understanding the structural and spectroscopic characteristics of the rotational isomers of methyl vinyl ketone are reported both for the electronic ground (S_0) and $n\pi^*$ excited state (S_1) and the potential energy curves for these states are plotted. It is found that while in the S_0 state, the molecule may exist in two stable conformational forms – *trans* and *cis*, in the S_1 state an additional *gauche* conformation with dihedral angle $C = C - C = 0 = \pm 90^0$ may also exist While in the ground state, the *trans* conformation is more stable than the *cis* by an enthalpy difference of 0 95 Kcal/mole, the reverse is true in the first excited state. Small values of enthalpy difference and rotational barrier (2.76 Kcal/mole) between the *trans* and *cis* conformers in the S_0 state suggest a significant concentration of about 27% of the higher energy *cis* conformer in this state. The S_1 states of the molecule both for *trans* and *cis* conformers are less polar than the corresponding ground states and explain the blue shift of $n\pi^*$ transition in a polar solvent The methyl group shows hindered rotation both in the S_0 and S_1 states with rotational barriers of 0.96 Kcal/mole and 0 45 Kcal/mole, respectively, in the *trans* conformers and 0 57 Kcal/mole and 0 72 Kcal/mole, respectively, in the *cis* conformers.

Keywords · Molecular orbital calculations, conformation, methyl vinyl ketone

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1. Introduction

Several molecular orbital [2,6-11], vibrational [14-18, 23], electronic [19-22] and microwave [4, 12, 13] studies have been reported for methyl vinyl ketone (MVK) in the literature. Discrepancies

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have however continued regarding the stable conformational forms of the molecule, their relative abundance and the assignments of their vibrational bands. Based on infrared and Raman spectral studies, Noack and Jones [12] suggested the existence of two conformational forms – *trans* and *cis* in MVK but were unable to predict their relative stability. While Dodziuk [7], on the basis of molecular orbital calculations using the Wiberg method, concluded that the *cis*-conformer is more abundant than the *trans*, Durig and Little [15], on the basis of vibrational spectral analysis in solid and gaseous phases, have concluded that the *trans* isomer is more stable than the *cis* by about 800 cals/mole. Not much information is available in the literature about the geometry and physico – chemical properties of methyl vinyl ketone in its excited electronic states. In order to answer questions related to the relative stability of the various conformers, their electronic spectra and physico-chemical properties in the ground and first excited n–π^* electronic states, we have conducted semiempirical molecular orbital calculations in the CNDO/2 and MNDO (AM1) approximations.

2. Method of calculation

Methyl vinyl ketone molecule (Figure 1) was considered as a two rotor system in which internal rotation may take place about the $C_1 - C_2$ single bond connecting its two completely asymmetric moieties $CH = CH_2$ and $O = CCH_3$ and also about the $C\text{-}CH_3$ bond. Thus, a number of conformations can theoretically arise for the molecule due to rotation about the two bonds. In order to obtain potential energy curve for asymmetric torsion in the two electronic states in the AM1 approximation (using computer programme MOPAC, version 6 [26]), the dihedral angle ϕ (C_3–C_1–C_2–O_4) was changed from 0° to 360° in intervals of 20° (intervals of 10° at the turning points). The SCF *ab initio* optimized geometry of *trans* acrolein [30], modified to include the methyl group, was used as initial geometry. Torsional potential analysis was conducted after optimizing this geometry at each stage of rotation by using the BFGS method [27]. Three fold potential function for the internal rotation of the methyl group about $C_2 - C_6$ bond was obtained by changing the dihedral angle $\phi(H_9C_6C_2C_1)$ in intervals of 20°. Electronic transitions and oscillator strengths were calculated in the CNDO/2 approximation using computer programme CNDUV99 [25] after taking into account configuration interaction between singly excited states.

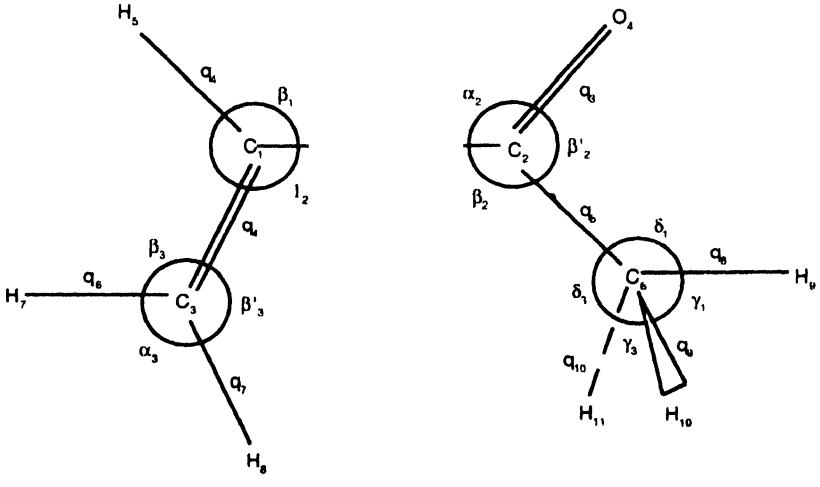

Figure 1. Numbering of atoms and definition of in-plane internal coordinates of methyl vinyl ketone molecule.

3. Results and discussion

3.1 Conformational studies :

Total energy for different conformations of MVK between $\phi = 0^{\circ}$ and $\phi = 360^{\circ}$ in AM1 approximation relative to the most stable conformers, *trans* for the ground and *cis* for first electronically excited states, were calculated and plotted in Figure 2 to give the potential energy curves. Some of the important parameters of the stable conformers, such as total

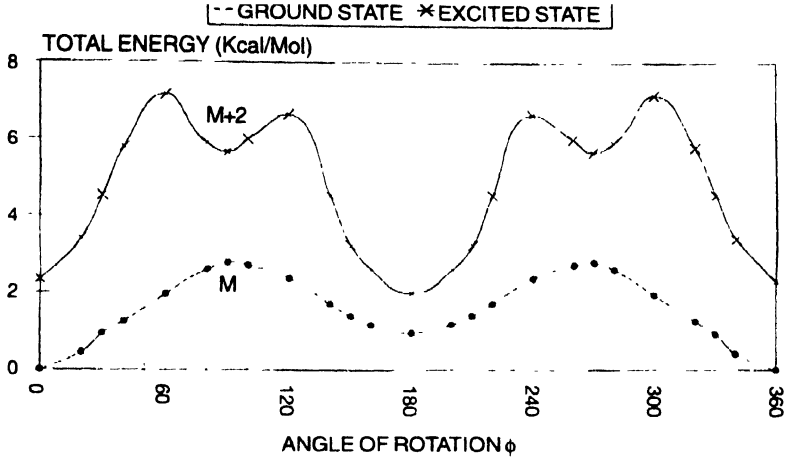

Figure 2. Potential energy curves of Methyl vinyl ketone in ground and first excited ($n\pi^*$) electronic states based on MO calculations The abscissa is the angle of rotation ϕ about the $C_1 - C_2$ bond relative to the *trans*- conformation for which the dihedral angle $C_3 = C_1 - C_2 = O_4$ is 180° The ordinate for the excited state ($M + 2$) is shifted by 2 00 Kcal/mole relative to the ground state (M).

energy, rotational barrier and enthalpy difference between the various stable conformers and ionization potentials, obtained from these calculations are given in Table 1. The total energy of the *trans* conformer, which is the most stable in the ground state is – 21178.99 Kcal/mole and that of the *cis* conformer, which is the most stable in the first excited state is – 21114.99 Kcal/mole.

As in the case of other similar molecules such as acrolein [31] and crotonaldehyde [29], it is found that the potential energy curves of the two electronic states of MVK can be fitted with potential function of the form :

$$2V = \sum_{n=1}^{6} V_n(1-\cos n\phi). \qquad (1)$$

The potential constants V_1 to V_6 of the ground state have values 0.7937, 2.1237, – 0.0871, –0.0106, 0.2397 and 0.1673. The corresponding values in the first electronically excited ($n\pi^*$) state are – 1.0233, 4.3058, 0.2204, 1.9793, 0.4803 and – 0.8379, respectively. Using potential constants in the relationships suggested by Margolin *et al* [34] the torsional frequency and the anharmonicity constant were calculated for the more abundant *trans* conformer in the ground state. The calculated value of the torsional frequency is 114.9 cm^{-1} which agrees with the experimental value 101 ± 2 cm^{-1} [13]. The anharmonicity constant for the torsional mode is

Table 1. Total energy, enthalpy difference, rotational barrier and ionization potential of conformers of methyl vinyl ketone in the ground and first excited electronic states in MNDO (AM1)

Ground state			Excited state		
Conformation		Total energy (Kcal/mole)	Conformation		Total energy (Kcal/mole)
I(t)	$\phi = 0°$	0.00[a]	I* (t)	$\phi = 0°$	0.32
II (C)	$\phi = 180°$	0.95	III* (G)	$\phi = \pm 90°$	3.63
			II* (C)	$\phi = 180°$	0.00[b]
Ionization potential (eV)			Ionization potential (eV)		
I(t)	$\phi = 0°$	10.65	I* (t)	$\phi = 0°$	3.95
II (C)	$\phi = 180°$	10.66	III* (G)	$\phi = \pm 90°$	3 38
			II* (C)	$\phi = 180°$	3 89
Rotational barrier (Kcal/mole)			Rotational barrier (Kcal/mole)		
II (c) / I (t)		1 82	III* / I*		1 49
I (t) / II (C)		2.76	I* / III*		4.80
			II* / III*		4.63
			III* / II*		1.00
Enthalpy difference (Kcal/mole)			Enthalpy difference (Kcal/mole)		
I (t) - II (C)		0.95	II* - I*		0 32
			II* - III*		3.63

[a] absolute value - 21178.99 Kcal /mole
[b] absolute value - 21114.99 Kcal /mole

found to be 4.5 cm^{-1}. Close agreement between calculated and experimental torsional frequencies confirm the finding of Pentin [28] that no more than six Fourier terms are necessary in the potential function eq. (1) for reproducing experimental results.

It may be seen from Figure 2 that in the electronic ground state MVK may exist in two stable forms – *trans* and *cis* ; the *trans* conformer being more stable than the *cis* by an enthalpy difference of 0.95 Kcal/mole (Table 1). Different values of enthalpy difference between the *trans.* and *cis* conformers varying between 0.48 and 3.1 Kcal/mole have been reported by different experimental methods [1,5]. Dodziuk [7] reported a value of 3.27 Kcal/mole from molecular orbital calculations based on Wiberg method which is a rather crude method. In a more recent publication, Durig *et al* [15], reported a value of 0.80 Kcal/mole for the enthalpy difference from vibrational analysis. Our calculated value of 0.95 Kcal/mole agrees with the findings of Durig and Little [15]. Similarly, our calculated value of *trans/cis* rotational barrier is 2.76 Kcal/mole which is in close agreement with the value 2.36 Kcal/mole reported by Durig and Little [15]. Dodziuk [7] and De Groot and Lamb [1] reported much higher values of 5.56 Kcal/mole and 8.4 Kcal/mole, respectively. The *cis/trans* rotational barrier is found to be 1.82 Kcal/mole which is in agreement with the experimental value 1.56 Kcal/mole [15].

In contrast to the ground electronic state, it follows from Table 1 and Figure 2 that in the first electronically excited state (S_1), the *cis* (II*) isomer is more stable than the *trans* (I*) by 0.32 Kcal/mole. This is close to the value 0.57 Kcal/mole reported by Pentin [28] from harmonic analysis of the two fold torsional potential. No experimental value is available in the literature to confirm our result. In between these two stable *cis* and *trans* conformations another stable conformation with dihedral angle $\phi = \pm 90°$ (*gauche*) may also exist. This *gauche* conformation

has an enthalpy difference of 3.63 Kcal/mole relative to the most stable *cis* conformer in the excited state. Although no experimental evidence is available in the literature for the existence of the *gauche* conformer in the first electronically excited state of MVK, such a conformer is reported to exist in identical molecules such as acrolein [31], crotonaldehye [29] and methacrolein [33]. The intramolecular perpendicular minimum in S_1 state has been reported to have a charge transfer (CT) nature due to the location of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) on the two different segments of the same molecule.

The rotational barrier between the *trans* and *cis* conformers in S_1 state is 4.80 Kcal/mole as against 2.76 Kcal/mole in the ground state (S_0). A similar increase in the potential energy barrier on excitation is reported in acrolein [31] molecule. The rotational barriers between the *cis/trans*, *gauche/trans* and *trans/gauche* conformers are 5.12, 1.49 and 4.80 Kcal/mole, respectively. Also, the rotational barrier between *cis* and *gauche* conformers is 4.63 Kcal/mole and between *gauche* and *cis* conformers is 1.0 Kcal/mole.

3.2 Methyl torsion :

Three-fold potential functions for the internal rotation of the methyl group, both for the *trans* and *cis* conformers of MVK, have been calculated for the S_0 and S_1 states. Total energy for different conformations of methyl vinyl ketone relative to *trans* and *cis* conformers are calculated and these are plotted in Figure 3(a) for the *trans* conformer and in Figure 3(b) for the *cis* conformer. It is found that the barrier to internal rotation of the methyl group in the *trans*

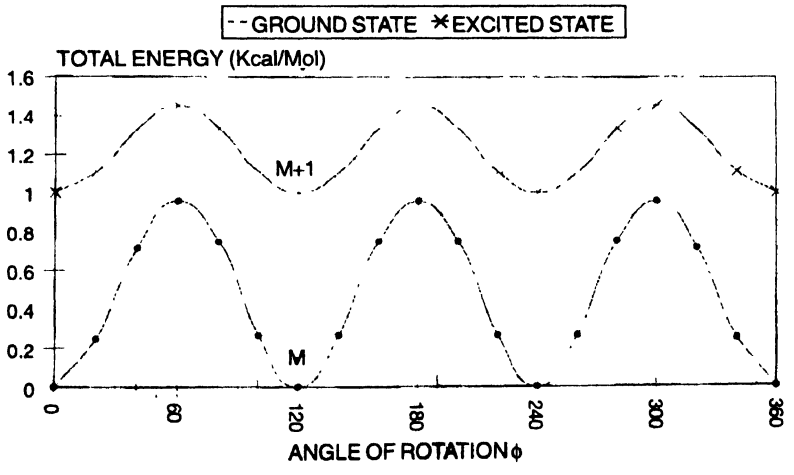

Figure 3(a). Potential energy curves of methyl rotation in *trans* Methyl vinyl ketone in ground and first excited ($n\pi^*$) electronic states based on MO calculations. The abscissa is the angle of rotation ϕ about the $C_2 - C_6$ bond for the *trans*-conformer, starting from dihedral angle $H_9C_6C_2O_4 = 0^0$. The ordinate for the excited state (M + 1) is shifted by 1.00 Kcal/mole relative to the ground state (M).

conformer is 0.96 Kcal/mole, in close agreement with the experimental value 1.25 Kcal/mole obtained by Foster *et al* [4] based on microwave studies. For the *cis* conformer, this value is 0.57 Kcal/mole. The potential barrier heights for internal rotation of the methyl group in the first excited state (S_1) are found to be 0.45 Kcal/mole (*trans*) and 0.72 Kcal/mole (*cis*). The potential energy curves in all the cases show a C_{3v} symmetry for the methyl group.

3.3 Ionisation potentials, population densities and dipole moments :

Using Koopmann's theorem, the ionization potentials obtained for the *trans* and *cis* conformers in the ground state are found to be 10.65 eV and 10.66 eV (Table 1), respectively. Our value for the *trans* isomer is close to the value 9.91 eV reported by Morrison *et al* [35] from electron

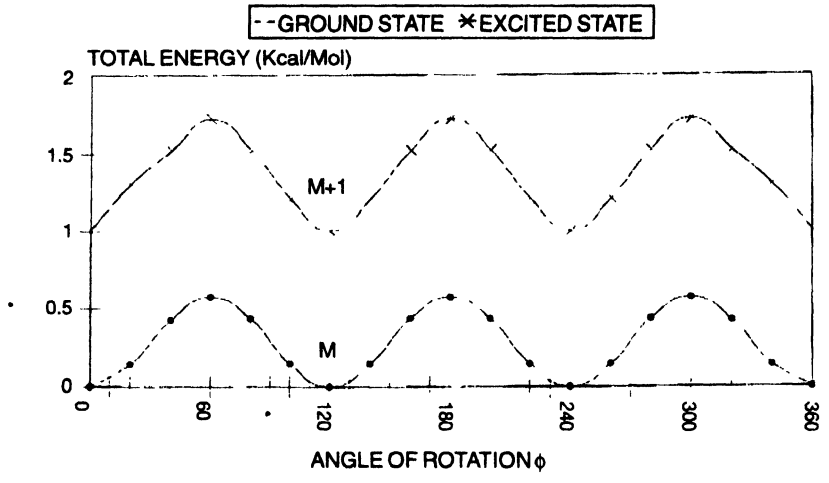

Figure 3(b). Potential energy curves of methyl rotation in *cis* Methyl vinyl ketone in ground and first excited ($n\pi^*$) electronic states based on MO calculations The abscissa is the angle of rotation ϕ about the $C_2 - C_6$ bond for the *cis*-conformer, starting from dihedral angle $H_9C_6C_2O_4 = 0^0$. The ordinate for the excited state (M + 1) is shifted by 1 00 Kcal/mole relative to the ground state (M)

impact method. The corresponding values of the ionization potentials in the first electronically excited ($n\pi^*$) state are 3.95 and 3.89 eV, respectively, and that for the *gauche* conformer is 3.38 eV. No literature is available to confirm our results for the *cis* conformer in the ground state and all the three conformers in the excited state.

The calculated atomic and bond population densities and dipole moments of the stable conformers of methyl vinyl ketone molecule in the ground and first electronically excited ($n\pi^*$) states are given in Table 2. A strong correlation is found to exist between the bond orders and bond lengths in the *trans* and *cis* conformers. An increase/decrease in bond length on electronic excitation, both in the S_0 and S_1 states, is accompanied with a corresponding decrease / increase in the bond order for all bonds like $C_1 - C_2$, $C_2 - C_6$, $C_1 = C_3$ and $C_2 = O_4$.

The calculated dipole moments of the *trans* and *cis* conformers of MVK in the ground state are 3.22 D and 2.68 D, respectively. Our calculated value for the *trans* conformer is very close to the experimental values 3.16 D [4] and 2.98 D [32]. The calculated values of the dipole moment of *trans*, *cis* and *gauche* conformers in the first electronically excited state are 1.85 D, 2.13 D and 2.28 D, respectively. No literature is available for the first electronically excited ($n\pi^*$) state. The redistribution of electrons makes the S_1 state of MVK less polar than its S_0 state, as may be seen from a lesser dipole moment 1.85 D for the *trans* conformer (I*) in the excited state as against 3.22 D in the ground state. Also, the dipole moment for *cis* isomer is 2.13 D in the excited state as against 2.68 D in the ground state.

Table 2. Atom and bond populations (q-values) and dipole moments for different conformations of methyl vinyl ketone in the ground and excited states in MNDO (AMI)

Ground state			Excited state			
	Conformation			Conformation		
Atom /Bond	I	II	Atom/Bond	I*	II*	III*
qC_1	6 2227	6.2475	qC_1	6.1217	6 1247	6 0759
qC_2	5.7499	5 7486	qC_2	6 0645	6 0734	6 1896
qC_3	6.1575	6 1246	qC_3	6.2597	6 2429	6 1973
qO_4	8 2893	8 2966	qO_4	8 1160	8.1070	8 1016
qH_5	0 8530	0 8682	qH_5	0 8511	0 8658	0 8608
qC_6	6 2686	6 2598	qC_6	6.1377	6 1343	6 1096
qH_7	0 8788	0 8855	qH_7	0.8722	0.8768	0 8729
qH_8	0.8846	0 8690	qH_8	0 8887	0 8768	0 8723
qH_9	0 8919	0 8976	qH_9	0 8957	0 8982	0.9010
qH_{10}	0 8997	0 9013	qH_{10}	0 8964	0 8999	0.9128
qH_{11}	0 8997	0 9013	qH_{11}	0 8963	0 9000	0 9115
qC_1–C_2	2 2121	2 2400	qC_1–C_2	2.5468	2 5333	2 2208
qC_1–C_3	3.8392	3 8095	qC_1–C_3	3 6222	3 6375	3 8604
qC_2–O_4	3.6259	3 5941	qC_2–O_4	3 1622	3.1412	3.2360
qC_2–C_6	2 8317	2 7775	qC_2–C_6	2 8953	2 8693	2 9511
μ (Debye)	3.22#	2.68	μ (Debye)	1 85	2 13	2 28

Experimental value 3 16D [4]

3.4 Electronic transitions :

Our CNDO/2 based transition energies and oscillator strengths for the *trans* and *cis* conformers of MVK are given in Table 3. Experimental measurements in a non-polar solvent isooctane show two absorption bands in the near UV region at 205 nm ($\log \varepsilon = 4.0$) and 331 nm ($\log \varepsilon = 1.38$). While the first band shows bathochromic shift to 212.5 nm ($\log \varepsilon = 3.85$) and 213 nm ($\log \varepsilon = 4.40$) in ethanol and water, respectively, the second band shows hypsochromic shift to

Table 3. Electronic transitions in *trans* and *cis* methyl vinyl ketone

Trans			*Cis*		
Exptl[a]	Calcd[b]	Assignment	Exptl	Calcd[b]	Assignment
λ nm ($\log\varepsilon$)	λ nm ($\log\varepsilon$)		λ nm ($\log\varepsilon$)	λ nm ($\log\varepsilon$)	
Singlet					
320.0 (1.32)	319.4 (0.76)	$n \cdot \pi^*$		313.4 (0.67)	$n - \pi^*$
212.5 (3.85)	212.6 (4.67)	$\pi \cdot \pi^*$		218.1 (4.41)	$\pi - \pi^*$
	171.7 (0.62)	$\pi - \pi^*$		172.6 (0.58)	$\pi - \pi^*$
	161.6 (3.46)	$\pi - \pi^*$		156.7 (4.28)	$\pi - \pi^*$

[a] In ethanol solution [19]. Corresponding values in isooctane are 331 nm and 205 nm and in water 308 nm and 213 nm [20].

[b] Based on CNDO/2 calculations

320 nm ($\log \varepsilon = 1.32$) and 308 nm ($\log \varepsilon = 1.50$), respectively in these two solvents. Hence, the absorption band at 205 nm has been assigned to $\pi - \pi^*$ transition and the 331 nm band to $n - \pi^*$ transition [20]. Our calculations confirm these assignments for the *trans* conformer and provide values 212.6 nm ($\log \varepsilon = 4.67$) and 319.4 nm ($\log \varepsilon = 0.74$), respectively. The corresponding transitions in the *cis* conformer have calculated values of 218.1 nm ($\log \varepsilon = 4.41$) and 313.4 nm ($\log \varepsilon = 0.67$), respectively. In addition, two more electronic transitions are predicted at 171.7 nm ($\log \varepsilon = 0.62$) and 161.6 nm ($\log \varepsilon = 3.46$), in the *trans* conformer which, as in other similar ketones [20], may be assigned to $n - \pi^*$ transitions. These bands in *cis* conformer appear at 172.6 nm ($\log \varepsilon = 0.58$) and 156.7 nm ($\log \varepsilon = 4.28$). No experimental data is however, available for the *cis* conformer.

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References

[1] M S de Groot and L Lamb *Proc. Roy. Soc. Lond.* **A242** 36 (1957)

[2] H Dodziuk *J. Mol Struct.* **20** 317 (1974)

[3] E V Sobolew and V T Aleksanian *Izv ANSSSR Ser. Khim.* 1336 (1963)

[4] P D Foster, V M Rao and R F Curl (Jr) *J. Chem. Phys.* **43** 1064 (1965)

[5] A J Bowles, W O George and W F Maddams *J. Chem. Soc.* **B810** (1969)

[6] J D Lewis, T B Malloy (Jr) T H Chao and J Laane *J Mol Struct.* **12** 427 (1972)

[7] H Dodziuk *J. Mol. Struct.* **20** 363 (1974)

[8] G Montaudo, V Librando, S Caccamese and P Maravigna *J Am. Chem Soc* **95** 6365 (1973)

[9] H Dodziuk *J. Mol. Struct.* **14** 343 (1972)

[10] H Dodziuk *J. Mol Struct.* **10** 275 (1971)

[11] L M Sverdlov, M A Kovner and E P Krainov *Kolebatelnyie Spektry Mnogoatomnykh Soiedinenji* (Nauka, Moskva) (1970) , P Cossee and J H Schachtsneider *J Phys. Chem.* **44** 97 (1966)

[12] K Noack and R N Jones *Can J. Chem.* **39** 2201 (1961)

[13] W G Fateley, R K Harris, F A Miller and R E Witkowski *Spectrochim. Acta.* **21A** 231 (1965)

[14] A Krantz, T D Goldfarb and C Y Lin *J. Am. Chem. Soc.* **94** 4022 (1972)

[15] J R Durig and T S Little *J. Chem. Phys.* **75** 3660 (1981)

[16] E A Cherniak and C C Costain *J. Chem Phys.* **45** 104 (1966)

[17] K Noack and R N Jones *Can. J. Chem.* **39** 2225 (1961)

[18] L N Bazhenova, G S Kopter, V I Tyulin, V M Tatevskii (USSR) *Vestn. Mosk. Univ. Ser 2 Khim.* **32** 14 (1991)

[19] *Spectrometric Identification of Organic Compounds* 3rd edn. R M Silverstein, Clayton G Bassler and Terence C Morrill p 244

[20] A E Moskvin *Theor. Exptl. Chem.* **2** (1966)

[21] R Luft *Bull. Soc. Chim. (France)* (1971)

[22] L J Gui Bault and G B Butler *J. Macro. Mol. Sci.* **5** (1971)

[23] H J Oelichmann, D Bougeard and B Schrader *J. Mol. Struct.* **77** 179 (1981)

[24] J A Pople and M Gordon *J. Am. Chem. Soc.* **89** 4253 (1967)

[25] CNDUV99 (QCMP 064) QCPE 333, Quantum Chemistry Program Exchange (Indiana University U.S.A.)

[26] MOPAC ver. 6.0 (QCMP 113) Quantum Chemistry Program Exchange (Indiana University, U.S.A.)

[27] C G Broyden *J. Inst. Maths. and Appl* **6** 222 (1970) ; R Fletcher *Computer Journal* **13** 317 (1970); D Goldfarb *Maths. Computation* **24** 23 (1970) ; D F Shanno *Maths. Computation.* **24** 647 (1970)

[28] Yu A Pentin *J. Mol Struct.* **46** 149 (1970)

[29] Sheela Thakur and V P Gupta *Indian J. Pure Appl Phys.* **36** 177 (1998)

[30] P Pulay, G Fogarasi, G Pongor, J E Boggs and A Varghe *J Am Chem Soc* **105** 7037 (1983)

[31] Sheela Thakur, V P Gupta and B Ram *Spectrochim Acta* **53A** (3) 749 (1997)

[32] L G Wessous *J Am. Chem. Soc.* **77** 4769 (1955)

[33] Sheela Thakur and V P Gupta *Indian J. Pure Appl. Phys* **30** 567 (1998)

[34] L N Margolin, Yu A Pentin, V I Tyulin *Opt I Spektr.* **40** 461 (1976)

[35] J D Morrison and A J Nicholson *J. Chem. Soc.* **20** 1021 (1952)